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C1A

(54) Ceramic coated graphite fiber and method of making same

(57) A graphite-precursor fiber is coated with a layer capable of forming a silicon-based ceramic on pyrolysis; and said graphite-precursor fiber and the layer thereon are copyrolysed at a temperature and for a time sufficient both to graphitize said fiber and pyrolyze said layer to said ceramic.

The invention also comprises a graphite fiber coated with a silicon-based ceramic layer.

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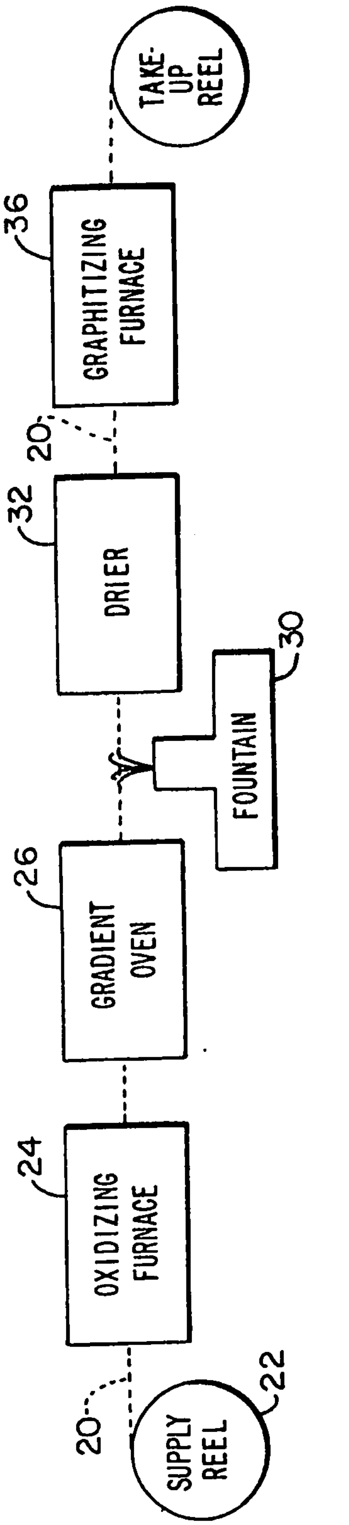

FIG. 1

SPECIFICATION

Ceramic coated graphite fiber and method of making same

This invention relates to oxidation-resistant graphitic fibers and processes for making same.

The high strength attributes of carbon or graphite fibers have made them valuable in forming composites with plastics, metals and ceramics. The last group is of interest because of the high temperature strength and low reactivity of ceramics. The addition of carbon or graphite fibers to ceramics can lessen the crack sensitive nature of ceramics and thereby broading their utility. There are a number of methods known in the art for combining graphite fiber with ceramic materials. For example, D. W. Bowes et al in U.S. Patent No. 3,646,908 describes a method of running a fiber through a vat of slurried ceramic particles. The particles cling to the fiber, and the combination is then layed up on a form. The form is then heated and pressed to fuse the ceramic. Another method is to chop the fiber and mix it with the ceramic for subsequent molding and fusing.

A general problem with these prior art methods is that ceramics generally fuse at high temperatures, and graphite, normally a very inert material, degrades at high temperatures as a result of combination with oxygen, a frequent component of ceramics. Another problem is that graphite fibers with a high Young's modulus have a fairly ordered surface due to the manufacturing process, but the exposed crystallite basal planes have low reactivity and bond poorly. These characteristics tend to cause shear separation between the fiber and ceramic matrix. Conversely, coatings that alloy themselves with the graphite may reduce or destroy the strength of the graphite. Also, coats that are thick can dominate the strength attributes of the combined materials. Finally, prior art ceramic coats on graphite fiber, either as a dried slurry or as a solid coating, tend to be brittle rendering the fiber difficult to work with.

A general solution to these problems has been to coat the fiber with silicon. Silicon readily bonds to carbon forming silicon carbide (SiC). Silicon also oxidizes to form a skin (SiO_2) that is both strong and will not oxidize even at high temperatures. To coat fibers with silicon, a variety of methods are known, such as vapor deposition, and dipping in molten silicon. Vapor deposition provides irregular results, while dipping leads to excessive conversion of the fiber surface to silicon carbide, thus weakening the fiber, and/or excessive silicon build-up serving to weaken the combination. In either case, thermal mismatch of the constituents can additionally lead to fiber shear decomposition.

A last, albeit important, consideration, is the depth of the silicon coat. The rule of mixture, that the strength of a composite is approximately equal to the sum of the component strengths times their relative proportion, implies that the coating should be as thin as possible, allowing the strength of the carbon to predominate.

The present invention generally concerns a silicon/carbon alloy fiber having excellent oxidation resistance and high mechanical properties, and the method of making such fibers. Such fibers are made in the present invention by coating a graphite-precursor fiber (PAN or stabilized PAN) with a coat comprising a polyorganosilicon. This coating and the graphite precursor are heat processed, i.e. pyrolyzed, simultaneously to convert the precursor to graphite and the coating to a silicon-based ceramic, thereby producing an alloy fiber. The latter demonstrates the mechanical properties of graphite fibers and the oxidation resistance of ceramic fibers.

Alternatively, the coating of polyorganosilicon may also include a pyrolyzable boron compound. Boron, the optional component in the coating, may be incorporated into the product at any of several different stages. For example, an alkylborate solution may be miscible with or used as the solvent for the polyorganosilicon, or a soluble boron compound can be applied in an additional dipping step prior to pyrolysis. A boron-containing gas can also be included in the atmosphere used during the final high temperature heat treatment to achieve copyrolysis causing graphitization of the precursor fiber and ceramic formation of the coating. In such case, pyrolysis of this coated precursor fiber yields a boron/silicon/carbon alloy fiber.

The copyrolysis of the precursor fiber and coating in the present invention is important for several reasons: the coating and fiber are in intimate contact throughout heat treatment, promoting good adhesion at the interface; a single heat treatment minimizes thermal exposure of the fiber; a single heat treatment is more economical in time, equipment and energy than multiple heat treatments; and residual stresses are minimized by the joint creation of the carbon core and the alloy coating.

Several recent and separate technological developments are useful in the present invention. Small (e.g. five micron) diameter graphite fibers have been developed from PAN (polyacrylonitrile) used as a graphite precursor. These small fibers demonstrate better mechanical properties, such as tensile modulus and strength, than thicker fibers. A relatively thick coating can be applied to these fibers without significantly degrading good fiber handling attributes in the resultant coated fiber; in particular, a small critical bend radius can be retained. A one micron thick coating on a four micron diameter fiber yields a six micron diameter fiber, which is nevertheless smaller than the typical seven microns of commercial graphite fibers.

Also, it has now been found that these thinner graphite fibers can be processed at lower temperatures to achieve high modulus. At typical temperatures for processing high modulus graphite fiber (e.g. 2300° C. to 3000° C., most ceramics exhibit a significant vapor pressure. For example, silicon dioxide starts to sublime at 2210° C. Using the thinner fibers allows ceramic processing of fibers to occur at lower temperatures while still resulting in adequately coated fibers with high modulus and oxidation resistance.

The organosilicon polymer technology developed by Yajima (S. Yajima, J. Hayashi, M. Omori, Chemistry Letters, pp 931-934, 1975) and West (U.S. Patent No. 4324901) is also useful in practising the present invention. Such organosilcon technology permits fabrication of ceramics from polymer precursors, utilizing the flexibility of the polymer in forming shapes prior to converting the polymer to a ceramic. Where the precursor polymer is a polycarbosilane, heat treatment above its decomposition temperature will convert the polymer to a polycrystalline silicon carbide. Polycarbosiloxanes tend to be thermally converted to polycrystalline mixtures of silicon oxide and silicon carbide. Use of this technology in the present invention permits silicon to be introduced into a graphite fiber system at relatively low temperatures and therefore in a low volatility manner. Low volatility is important to insure high coating yield during graphitization firing.

As detailed in the following examples, the combined treatment with silicon and boron yields a substantial and unexpected improvement over either treatment alone. Although the combined treatment is particularly effective when applied to smaller diameter fibers, it is not limited to such but is applicable to larger carbon or graphite fibers.

Accordingly it is an object of the present invention to provide a ceramic/carbon alloy fiber (or a graphite fiber coated with ceramic bonded thereto). It is a further object of the present invention to provide a method of producing such a fiber by copyrolyzing a graphite-precursor fiber coated with a polymeric ceramic-precursor material.

Further objects of the present invention are to provide a graphite fiber with improved resistance to oxidation, to provide a ceramic surface coating on graphite fibers to resist oxidation of the fiber, and to form such a ceramic surface coating on a carbon or graphite fiber without substantially reducing the tensile and handling properties of the fiber.

Yet other objects of the present invention will in part be obvious and will in part appear hereinafter. The invention accordingly comprises the processes comprising the several steps and relation of one or more of such steps with respect to each of the others, and the products and compositions possessing the feature, properties and relation of elements, all of which are exemplified in the following detailed disclosure and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein there is shown as schematic apparatus useful in carrying out the processes of the present invention.

In the process of the present invention, tow 20 of fibers of graphite-precursor material, such as pitch, rayon or the like, but preferably polyacryonitrile (PAN) is fed from supply reel 22 to furnace 24. The term PAN as used herein should be understood to mean and include both the acrylonitrile homopolymer, and the various copolymers of acrylonitrile with up to 15 mol percent of styrene, vinylpyridine, vinyl chloride, vinylidene chloride, acrylic acid methyl ester, methacrylate esters, vinyl acetate, and others. Tow 20 is typically formed of several hundred or more parallel, continuous filaments each having a nominal average diameter of, for example, ten microns. In furnace 24, the tow is held under tension, typically from 5 to 100 grams per square millimeter of fiber cross sectional area, so as to align the carbon structure and draw the fiber to a narrower diameter. While under tension in furnace 24, the fiber is continuously oxidized in an oxidizing atmosphere, such as air, at from about 200 to 300 degrees C over a period of time, for example 120 minutes, until it acquires an oxygen content of between about five to fifteen weight percent, preferably about ten percent. This standard procedure for strengthening PAN fiber before further processing is known as stabilization, or thermosetting.

The stabilized fiber is then fed into gradient oven 26 wherein it is continuously heat treated in a non-oxidizing atmosphere, typically nitrogen or the like, while under tension of from about 500 to 5000 grams per square millimeter of fiber cross-sectional area. The entrance temperature to oven 26 is maintained at about 300° C., while the exit temperature of the oven is about 650° C. The residence time of the fiber in oven 26 is nominally five minutes. Under these conditions, the PAN fiber tow is carbonized and drawn down to a desired minimum diameter.

As noted above, an essential part of the process of the present invention is the provision on the carbon-precursor fiber of a coating of polyorganosilicon as a silicon-based ceramic precursor. Among the polyorganosilicon compounds useful in the present invention for this purpose are polysilanes such as polydimethylsilane and polysilastyrene; polysiloxanes such as polyphenylmethylsiloxane and poly-dimethylsiloxane; polycarbosilanes such as $(\mathrm{Si{-}C})_n$—polycarbosilane, polysilazanes such as

$$\left(-\underset{Me}{\overset{Me}{\mathrm{Si}}}-\underset{H}{\mathrm{N}}-\right)_n$$ —polydimethylsilazane and polyphenylmethylsilazane;

and polysilithianes such as polydimethylsilithiane and polyphenylsilithiane; and the like. Such compounds must be either coatable per se onto the fibers or be coatable from solvents onto the fibers, and the coating formed must be capable of being pyrolyzed into a silicon-based ceramic within the temperature range (i.e. ca. 1000° to 2550°C) at which the graphite-precursor fiber pyrolyzes to graphite. In a preferred embodiment of the present invention, the PAN fiber is continuously coated with a polyorganosilane, such as a polysilastyrene formed by reacting phenylmethyldichlorosilane and dimethyldichlorosilane as taught in U.S.

Patent No. 4,324,901, and having a molecular weight typically in the range of from 500 to 50,000, and preferably about 1500. The coating can be applied to the tow either before or after carbonization of the PAN has been achieved, simply by passing the tow through fountain 30 of the polyorganosilane in any of a number of relatively volatile solvents such as toluene, xylene, tetrahydrofuran and the like. The polyorganosilane coating adheres to the fiber tow, penetrating the pores and surface irregularities of the latter, providing a coat with a depth of two or three microns.

The coated fiber tow is preferably passed through drier 32 in a non-oxidizing atmosphere, such as nitrogen, held at approximately 250° C. Such drying serves to evaporate most of the volatile solvent, and shrinks the polymer coating on the tow to approximately one or two microns in thickness. This drying step need not be provided for all coating materials inasmuch as some may not use a solvent and in other instances, some solvents may simply be vaporized or decomposed (without detrimental effects to the ultimate product) directly by the subsequent high temperature heat treatment to which the coated tow will be subjected.

Lastly, the polymer-coated fiber tow is continuously passed through graphitizing furnace 36 in a non-oxidizing atmosphere such as nitrogen and slowly heated to temperatures between 2100° and 2500°C, so as to be resident in the furnace for a time sufficient to substantially copyrolyze both the PAN fiber to graphite and the polyorganosilicon coating to a silicon ceramic. Typically for the preferred poysilastyrene coating on PAN, carbonzation is readily achieved with a residence time of from five seconds to one minute at 2300°C. During this period, any remaining volatiles in the PAN, polysilane or solvent are driven off and a silicon-based ceramic coating is formed. The ceramic coating intimately mates to and fills the pores and irregularities in the underlying graphite to assure substantial sealing of the fiber surfaces. Some chemical reaction is believed to occur at the ceramic-graphite interface forming some silicon carbide.

It should be noted that the choice of temperatures used in furnace 36 during pyrolyzation depends on several variables and may be changed from those stated above. Of course, it is necessary to be at or above the minimum temperature, i.e. 1000° C, at which graphitization will occur. Similarly it is important to not exceed the minimum temperature, i.e. ca. 2550° C, at which the ceramic starts to break down. Within this temperature range of 1000 to 2550° C, copyrolyzation of the polyorganosilicon coating must occur while the latter is still in contact with the fiber. Thus the temperature selected must be sufficient to insure thermal decomposition of the coating to a ceramic before the coating can evaporate or vaporize and the graphitization process must be completed at a temperature and/or in a time period selected to insure that no substantial amount of the ceramic coating evaporates or sublimes.

In some instances, it is desirable to add boron-ceramic precursor materials to the coating either before or in the early stages of pyrolysis. For example, one can add a gas mixture of a boron halide, such a boron chloride or boron bromide and a hydrocarbon gas such as methane and the like, that then react in the pyrolyzation heat to deposit boron. Diborane gas may also be used as a source of boron. The fiber tow may be also coated by dipping it into a borate salt solution such as an aqueous solution of boric acid or ammonium borate either before or after coating with the polyorganosilicon and prior to graphitization. Alternatively, one may mix an alkylborate solution with the polyorganosilane, for example by using methyl borate as a solvent for polyorganosilane, prior to coating the tow with the latter. The boron-containing material added to the coating should be pyrolyzable to yield boron or a reaction product or boron with carbon and/or silicon, at the same temperature used to copyrolyze the graphite precursor and silicon-based ceramic precursor coating.

Oxidation resistance of the coated fibers serves as a measure of the time that might be available for mixing such fibers with ceramics or metals while at a high temperature to form ceramic/fiber or metal/fiber composite materials. Oxidation resistance also serves as a measure of the fiber durability under high temperature service conditions. Fibers, treated according to the present invention and with other coatings and processed at different temperatures, were tested for oxidation resistance under different stress loads in terms of time to failure. The results shown in the following tables thus reflect the relative utility of these fibers for use in ceramic/fiber or metal/fiber composites.

Table I shows the measured time to failure in minutes and seconds for variously treated graphite fibers held at 900°C in air under a 3.5 gram load.

TABLE I

Fiber Treatment

Process Temp.	None	Methyl Borate	Polysilane	Polysilane and Methyl Borate
2100°C	–	8:10	6:39	–
2200°C	–	32:16	8:14	–
2300°C	0:55	43:41	16:00	38:20
2400°C	–	29:10	14:27	–
2500°C	2:09	37:41	4:25	4:03

Table II shows the measured time to failure in minutes and seconds for graphite fibers originally processed at 2300°C after various coating treatment, and now tested in air at 900°C under loads of 40 grams and 100 grams.

TABLE II

Fiber Treatment

Load in Grams	None	Methyl Borate	Polysilane	Polysilane and Methyl Borate
40	0:20	18:18	12:04	25:27
100	0:17	13:58	9:22	15:35

It is evident that the polyorganosilane coating significantly increases the oxidation resistance of the fiber as against untreated fiber. But Table I also indicates that using methyl borate together with the polysilane coating dramatically improves oxidation resistance of the graphitic fibers. Again, Table II, based on pyrolysis done at the optimum processing temperature of 2300°C, confirms the improvements gained in oxidation resistance by treatment with polysilane and particularly with the combination of polysilane and methyl borate, over those fibers treated with methyl borate alone or subjected to no coating treatment.

Additional tests further indicate that the graphite fibers of the present invention coated with either silicon ceramic or boron/silicon ceramic have substantially similar thermal conductivity, appearance, flexibility, tensile strength and chemical resistance to uncoated graphite fibers made by otherwise identical treatment, while also exhibiting the desired substantially improved oxidation resistance compared to uncoated fiber.

Since certain changes may be made in the above process and the product thereof without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not in a limiting sense.

CLAIMS

1. A process of forming a ceramic coated graphite fiber with improved oxidation resistance, said process comprising the steps of,

coating a graphite-precursor fiber with a layer capable of forming a silicon-based ceramic on pyrolysis; and

copyrolyzing said graphite-precursor fiber and the layer thereon at a temperature and for a time sufficient both to graphitize and fiber and pyrolyze said layer to said ceramic.

2. A process as defined in claim 1 wherein said step of copyrolyzing is carried out in a non-oxidizing atmosphere and at a temperature between about 1000° to 2550° C.

3. A process as defined in claim 1 wherein said fiber is a material selected from the group consisting of polyacrylonitriles, coal tar pitch and petroleum, and rayon.

4. A process as defined in claim 1 wherein said layer comprises a polyorganosilane.

5. A process as defined in claim 4 wherein said polyorganosilane has a molecular weight in the range of from 500 to 50,000.

6. A process as defined in claim 1 wherein said layer also includes a material capable of being pyrolyzed at said temperature and during said time into boron.

7. A process as defined in claim 6 wherein said material comprises an alkylborate.

8. A process as defined in claim 2 including the step of providing a boron halide and a hydrocarbon fluid to said atmosphere during at least the initial stage of said step of copyrolyzing.

9. A process as defined in claim 1 including the step of preoxidizing said fiber prior to said step of coating, by heating said fiber in an oxidizing atmosphere at a temperature and time sufficient to oxidize said fiber to include a weight percent oxygen in the range of from 5 to 15.

10. A graphite fiber coated with a ceramic layer formed of material produced by the copyrolysis of a graphite-precursor fiber with a polyorganosilicon coating thereon.

11. A graphite fiber as defined in claim 10 wherein said layer also includes material produced by the copyrolysis of a boron-containing compound.

12. A graphite fiber coated with a silicon-based ceramic layer.

13. A graphite fiber as defined in claim 12 wherein said ceramic layer is also boron-based.

14. A process of forming a ceramic coated graphite fiber as claimed in any one of claims 1 to 9, substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

15. A graphite fiber coated with a ceramic layer as claimed in claim 10 or 11, substantially as hereinbefore described.

16. A graphite fiber coated with a ceramic layer as claimed in claim 12 or 13, substantially as hereinbefore described.

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